SOLVATED ELECTRON TECHNOLOGY FINDINGS AND RECOMMENDATIONS BY NFESC TECHNOLOGY APPLICATION TEAM

Technology Description

The Solvated Electron Technology (SET) Process is a method of reducing halogenated hydrocarbons in a mixture of sodium or other alkali metal in liquid ammonia. In actual practice, pieces of anhydrous sodium or potassium are added to liquid ammonia at about 100°C and the resulting colorless ammonia solution turns blue. The blue color is due to the solvated electrons in the mixture. As sodium dissolves in ammonia it decomposes into sodium ions (Na⁺) and electrons (e⁻) as follows:

$$Na^0 + {}_{anhydrous} NH_{3 liquid} \rightarrow Na^+ + e^-_{(blue color liquid)}$$

The solvated electrons in solution act as powerful reducing agents. This method can be used to strip chlorine atoms from small amounts of chlorocarbons, such as TCE, PCB, and DDD, DDE, DDT, dieldrin, and chlordane.

Commodore Solution Technologies, Inc. of Marengo, Ohio, has demonstrated the SET process at laboratory (1 liter size), pilot (30 to 55 gallon sizes), and commercial (10 ton per day system) scales to establish efficacy of this technology. The results from most of these demonstrations are discussed in Attachment A. SET technology is effective in treating soils, sludges, and oils contaminated with PCBs, pesticides, RCRA metals, and other organics. For full scale clean ups, the existing SET pilot scale units should be scaled up to larger sizes such as ten tons per day (Commodore's S-10 unit). Since the process utilizes anhydrous ammonia and sodium, both of which are highly reactive, commercial operations of SET require large quantities of these materials at the site, posing serious health and safety issues and concerns, all of which need to be accounted for while using this technology. Although SET is a contractor-owned and operated system, its operation at a Navy installation does not relieve the Navy from liability issues.

Analysis of Demonstration Data

Based on the discussions of each demonstration listed in Attachment A, the data proved inconclusive to answer the following concerns and issues:

- 1. Since liquid ammonia is unable to penetrate wood or concrete, this technology cannot treat contaminants lodged in such materials. These materials will require crushing or shredding prior to treatment. However, at the Weldon Springs site (Project #3 of Attachment A), the corncobs actually absorbed ammonia which increased its consumption, and hence the treatment costs.
- 2. The reduction of halogenated materials from soils, oily wastes, sludge, and sediments requires almost complete removal of moisture through pre-drying. This is because liquid ammonia reacts quickly with water to form ammonium hydroxide, which is not only exothermic, but also inhibits production of solvated electrons. The sodium metal

- also has affinity for water to form sodium hydroxide, that could result in an under kill of contaminants. Therefore, a precise qualitative analysis of the contaminants in the matrix is required before treating it with the SET process.
- 3. When treating large volumes of wastes containing TCE and other chlorocarbons, SET would produce large quantities of hydrocarbons with a given vapor pressure. According to Dalton's Law of partial pressures, the ammonia and the other gas or vapor pressure are additive. pressure relief valves and permits for accidental venting of ammonia into the air. Pressure relief valves and permits for accidental venting of ammonia into the air would be required as a result of the pressure rise within a closed system. This could be a concern with large size unit such as Commodore's S-10, which has not yet been field demonstrated.
- 4. The test results to date fail to establish that the sodium will not produce toxic byproducts. For instance, sodium amide produced during the reaction could convert chlorinated compounds such as chlorobenzene into amines, which are toxic. However, the chemistry of this process is very complex to actually predict the final products, therefore, the nature of by-products produced were not examined. This could be a concern when treating wastes which contain a variety of contaminants.
- 5. Since the solvated electron reaction is highly exothermic in nature, the use of this technology for treating wet soil or sludge on a large scale could have safety, health, and environmental issues, all of which should be considered when designing and operating a working system. However, in the studies reviewed by the technology application team (TAT), no significant health and safety problems were reported.
- 6. The solvated electron solution is highly corrosive, which could impact structural integrity of the SET reactor and other components. This critical factor must be accounted for properly while designing and operating a commercial-scale unit.
- 7. A partial decomposition of target contaminants, either due to insufficient amounts of reagents such as sodium or ammonia in the reactor, or due to the presence of other reactive metals, such as iron in the matrix being treated, could affect the performance of the process.
- 8. Ammonia vented into the atmosphere to control over pressurization may attract horse flies, posing health issues at the site. This minor issue can be solved easily by the installation of adequate screens at the site.
- 9. No data on the public reaction to commercial operation of a SET unit has been documented to date, but could become an important factor for using this technology in certain states such as Hawaii.
- 10. The limited cost information generated during various demonstrations showed that SET is more costly than other competing technologies. However, comprehensive cost data to analyze the economics of SET are unavailable.

Regulatory Issues

Accidental venting of ammonia to relieve pressurization in the system could lead to the following issues:

- a) The need for a permit for ammonia release into the atmosphere.
- b) Health and safety issues regarding the use of large quantities of ammonia and sodium at the site. This is analogous to operating a small chemical plant at the site and therefore would require an emergency response system and procedures in case of an accident or spills.
- c) Health issues related to ammonia attracting horse flies at the SET site.
- d) Commodore has operated under an R D and D permit at their Marengo facility.
- e) Commodore holds a nationwide TSCA permit.

Competing Technologies

Other technologies competing with SET include thermal desorption (such as thermal blankets), soil flushing or solvent extraction, and incineration. Thermal desorption appears to be promising, but due to the existence of a limited market for these types of technologies, the commercialization is very slow. The data to prove that soil washing or solvent extraction can reduce PCBs to less than 2 ppm is insufficient. Incineration, on the other hand, is well established but is not favored by the regulators and is also energy intensive.

Commodore SET Units

Various field demonstrations conducted by Commodore to date have established that the SET process is capable of remediating PCBs in soils, sludges, and oils to below 2 ppm, and is also effective in treating soils contaminated with pesticides.

Laboratory units - D1 and D2 demonstration units treat 1 liter per batch.

Pilot Scale Units - S 4 500-lbs per batch unit, US EPA permitted.
- L1200 treats 55 gallons of liquids per batch.

Commercial Size Unit - S 10 treats 1 ton per hour with 10 tons per day capacity.

Team Findings and Recommendations

Various field demonstrations conducted by Commodore have established that the SET process is one of the very few available technologies with demonstrated capability of treating PCBs in soils, sludges, and oils to less than 2 ppm. The technology is also effective in treating soils contaminated with pesticides. No one competing technology appears to have an edge over SET. Therefore, when evaluating options for a site that requires treatment to very low levels, SET should be considered as one of the few viable alternatives. The evaluation of the demonstration data also revealed that detailed SET cost information for the is unavailable. Efforts should be directed to identify Navy and Marine Corps needs for this technology before proceeding with developing detailed SET cost information.

ATTACHMENT A

Listing of Commodore's Solvated Electron Technology Demonstrations

Project No. 1: New Bedford Harbor Superfund Site, New Bedford, Massachusetts

POC: Bill Hines, Resource Conservation Company (RCC), Seattle, Washington (425) 828-2400

Project Description: This on-site treatability study (1995) used a 1-liter sized demonstration SET unit to process PCB contaminated sludge dredged from the bottom of the Acushnet River. The test results showed that the PCB concentrations approaching 20,000 ppm in the sludge were reduced to less than 5 ppm. Commodore performed this study under subcontract to RCC, who was under contract to Foster Wheeler Environmental Corporation.

Project Status: Prior to starting the treatability study public reaction did not favor burying the sludge in a landfill. However, after the treatability study, the public reaction to dig and haul became favorable to burying the contaminanted sludge. Therefore, the SET was not used for the actual clean up of the soil.

Project No. 2: Empire States Electric Energy Research Council, New York, New York

POC: Rich Hixon, New York (518) 370-5631

Project Description: This treatability study was conducted in 1997 using an S-4 (55-gallon drum) pilot SET unit to conduct tests on PCB contaminated soils from a transformer spill site in upstate New York. The study was performed at Commodore's facility in Marengo, Ohio. The test results showed that the SET process reduced the PCBs concentrations in the soil from about 1,000 ppm to less than 2 ppm and the RCRA metals in the soil were also reduced substantially. For this project Commodore was under contract to Flour-Daniel GPL.

Project Status: The purpose of this project was to generate information for the electric utilities to consider SET for future clean up projects. It was concluded that SET is not competitive with landfilling except under certain instances such as, where transport through sensitive areas, avoidance of lingering liability, characteristics of soil require onsite treatment, or if the SET process is part of a treatment train. The SET is applicable if the soil contains other waste streams not suitable for landfilling.

Project No. 3: Weldon Springs Site Remedial Action Project, St. Louis, Missouri

POC: Tom Pauling, DOE, St. Louis, Missouri (314) 441-8086

Project Description: This demonstration, concluded in 1998, was a commercial application of SET using the S-4 unit to process about 10,000 pounds of sludge waste containing organic absorbents (corn cobs), oil, and metals contaminated with PCBs, radionuclide source material, and various RCRA materials. MK had originally intended to send the waste to a DOE incinerator, but found that the facility accepted only liquid wastes. Also, while preparing the sludge for shipping, MK added corncobs to the sludge to facilitate shipping. Commodore sent an S-4 unit to the site that was too small and not the best design to treat this type of waste. Due to the corncobs, Commodore experienced problems mixing in the reactor. Shredding equipment was utilized to facilitate the reaction to bring the PCB concentrations down to acceptable levels. Once the target level of 2 ppm was reached, regulators permitted disposal into a specially constructed cell for the radioactive wastes.

Project Status: Commodore's goal was to obtain an EPA permit for the SET process. The EPA was also on-site to collect split samples for analysis. The test results indicated that the SET process could achieve 2 ppm clean up standards for the PCBs. One other problem caused by the corncobs was that they entrained ammonia, which increased ammonia consumption significantly. DOE does not have immediate plans to use this technology for similar clean up tasks.

Project No. 4: Ogden Environmental and Energy Services, San Diego, California

POC: Ms. Kyle Olewnik, Ogden Environmental and Energy Services Company, San Diego, California (619) 458-9044

Project Description: This treatability study to process PCB contaminated soils from the Naval Radio Transmitting Facility site in Oahu, Hawaii, was conducted by Commodore in 1999. The study was performed at Commodore's facility in Marengo, Ohio, using a 1-liter sized, laboratory scale unit. A total of five soil samples were treated; two of which did not meet the 1 ppm standard for PCBs in the treated samples. These two samples contained PCB levels up to 10,000 ppm, and were pretreated with ammonia to meet the 1 ppm clean up criteria. The soil samples that did not require pretreatment contained PCB concentrations ranging from 100 to 4,000 ppm.

Project Status: Ogden Environmental and Energy Services Company recommended that two technologies, In Situ Thermal Desorption and the Solvated Electron Technology Process, should be tested on a pilot scale on site to gather additional information before selecting a technology for the site clean up.

Project No. 5: Pennsylvania Air National Guard, Harrisburg, Pennsylvania

POC: Matthew Alexander, Operational Technologies Corporation, San Antonio, Texas (210) 731-0000

Project Description: This treatability study was conducted in 1999 by Commodore using laboratory (1 liter) and pilot scale (S-4, 55 gallon) units on soils from Pennsylvania Air National Guard. The study was performed at Commodore's Marengo facility under contract from Operational Technologies Corporation, a contractor to the Air National Guard. The test samples contained PCB concentrations of 1,000 ppm or less. The soil samples contained about 10% moisture and therefore required dry processing to meet clean up standards of 1 ppm of PCBs.

Project Status: The test results concluded that the SET met the clean up standards for PCBs of 1ppm. The Operational Technologies Corporation, after comparing SET with Soil Flushing and Thermal Desorption, recommended it as the technology of choice for full scale clean up. The full scale clean up using the S-10 (10 tons per day) unit is due to start in late 1999.

Demonstrations Under US EPA Cognizance

POC: Winston Lue, US EPA, Washington, DC (202) 260-3962

Commodore has demonstrated the SET process to the US EPA several times. Commodore holds a nationwide permit for mobile units for processing PCB contaminated soils and oils including metals and organics. Demonstrations conducted by Commodore under US EPA cognizance are listed below:

- 1. New Bedford Harbor Superfund Site, New Bedford, Massachusetts (1995). See Project No. 1.
- 2. National Test Site, Port Hueneme, California (1996). Treatability studies on a laboratory scale (1 liter) unit to treat PCB containing soils and oils and pesticide-contaminated soils. The test results showed that most test runs met clean up standards.
- 3. Empire States Electric Energy Research Council, New York, New York (1997). See Project No. 2.
- 4. Weldon Springs Site Project, St. Louis, Missouri (1998). See Project No. 3.
- 5. Pennsylvania Air National Guard, Harrisburg, Pennsylvania (1999). See Project No. 5.